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Coupled cluster evaluation of the second and third harmonic scattering responses of small molecules

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Introduction and objectives

The interaction between an electric field (\vec{F}) and a molecular system induces a dipole moment:

$$\Delta\vec{\mu}(\vec{F}) = \alpha \cdot \vec{F} + \frac{1}{2!} \beta : \vec{F}^2 + \frac{1}{3!} \gamma : \vec{F}^3 + \dots$$

where α is the polarizability (rank 2 tensor) and β, γ are the first and second hyperpolarizabilities (rank 3 and 4 tensors). The experiments rely on relative rather than absolute measurements, which requires precise knowledge of the response of these reference compounds. β_{SHS} was already investigated for different systems,¹ but there are only TWO recent experimental studies for γ_{THS} by Van Steertegem *et al.* and Rodriguez.²

The goals of this work³ are:

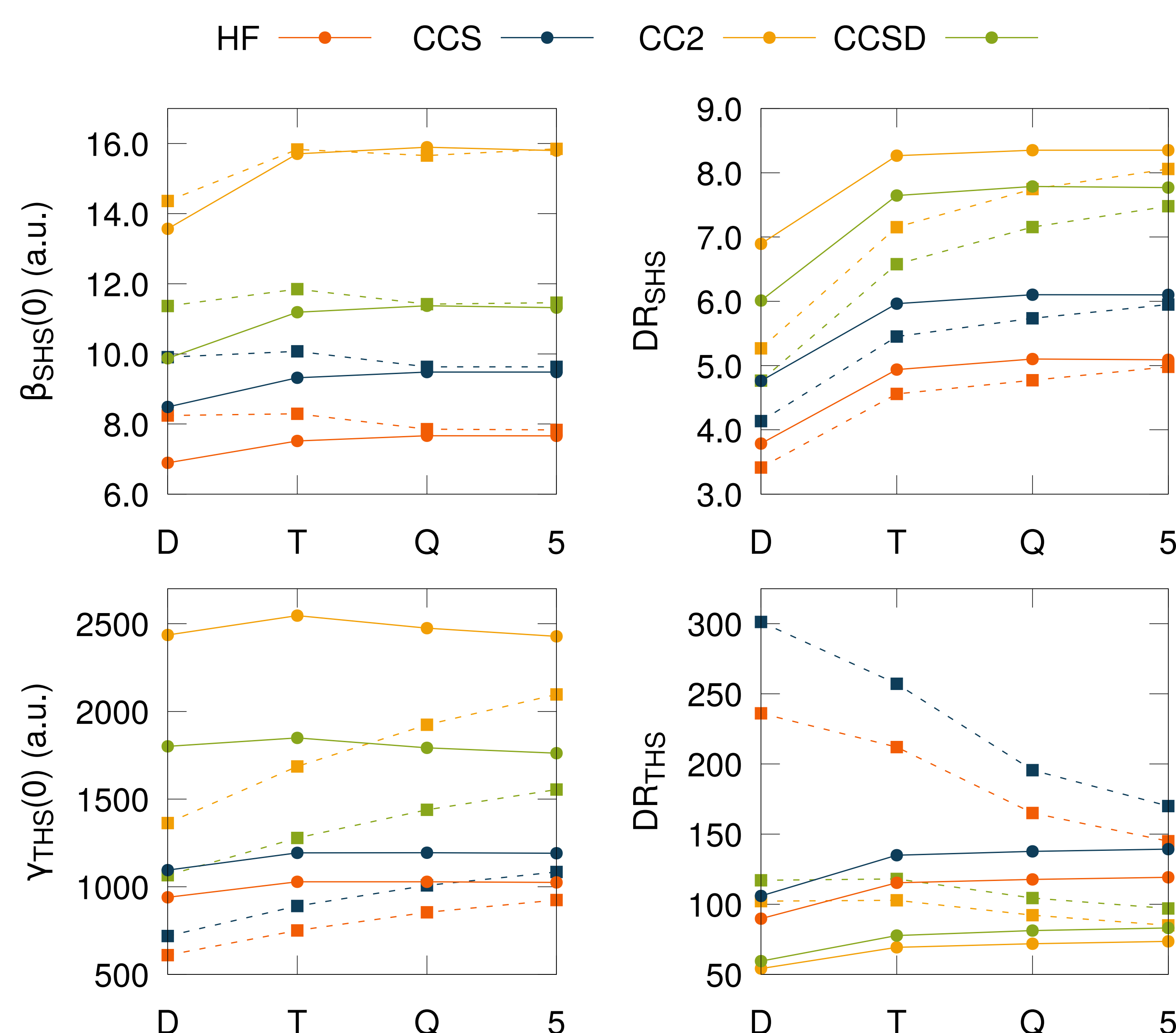
- The definition of reference values. 6 molecules were selected: H₂O, CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄ and CH₃CN;
- The definition of an appropriate level of approximation since it is the first quantum chemistry investigation on γ_{THS} ;
- To establish structure-activity relationships, the calculation and interpretation of the irreducible spherical components.

Computational details

Geometry optimized at the M06/6-311G(d) (water) and MP2/cc-pVTZ levels. Gas phase hyperpolarizabilities computed with Dalton 2016, with a hierarchy of coupled cluster methods (CCS, CC2, CCSD), in combination with quadratic/cubic response functions⁶ and (d-)aug-cc-pVXZ basis sets to check basis set convergence.

Results

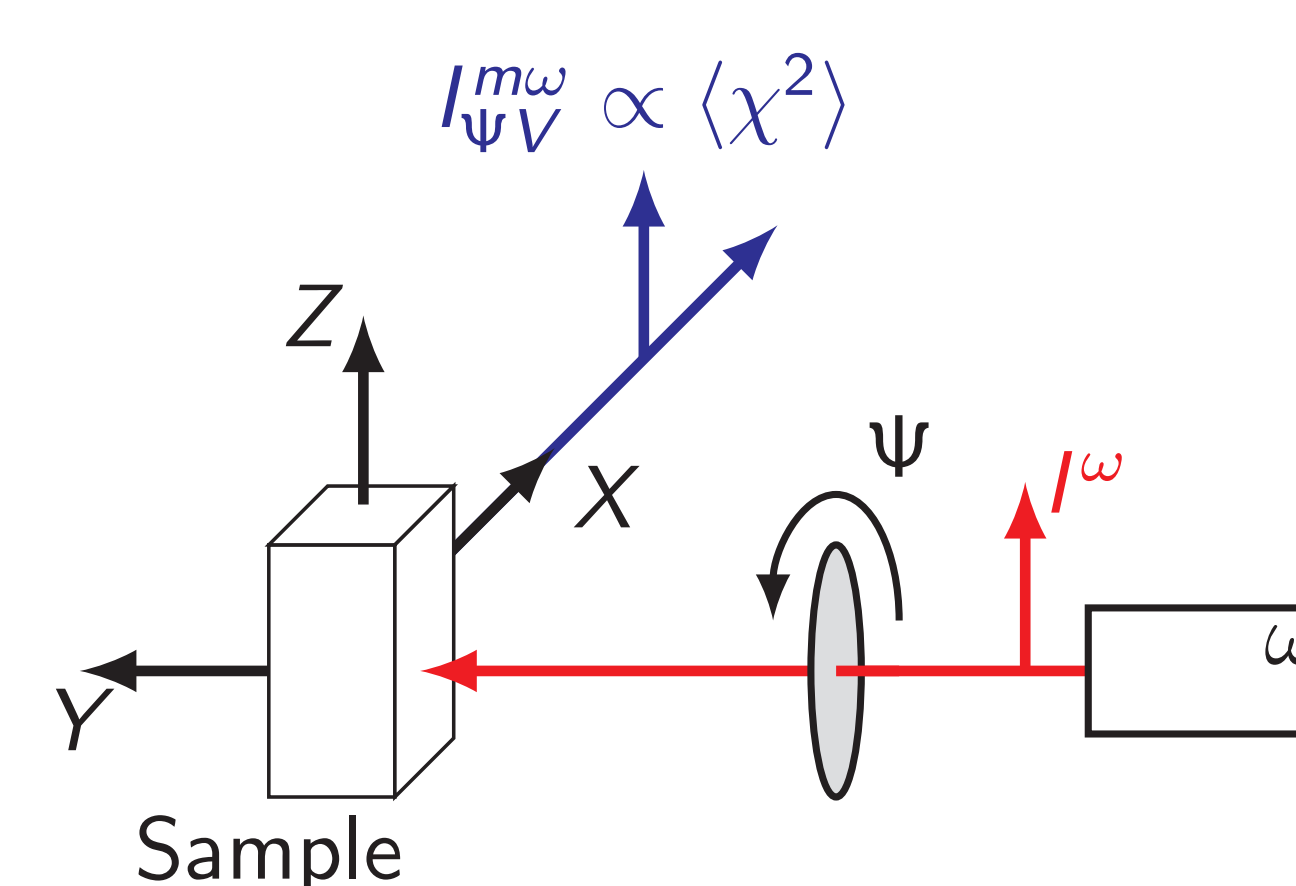
- Impact of the basis set (d-aug-cc-pVXZ in plain, aug-cc-pVXZ in dashed) and of the method on the static first and second hyperpolarizabilities of water:



Substantial electron correlation and basis sets effects are evidenced (especially for DR_{THS}), but the effect seems less important for the other molecules: the CCSD/d-aug-cc-pVDZ level was selected. Note that the impact of CC3 is negligible with respect to CCSD.

- Static CCSD/d-aug-cc-pVDZ results for the six reference molecules: dipolar character of β_{SHS} increase from CCl₄ to H₂O, and γ_{THS} dominated by its isotropic ($J = 0$) contribution, followed by its quadrupolar ($J = 2$) contribution.

SHS and THS measurements



Geometry	$\langle \chi^2 \rangle$	
	$m=2$	$m=3$
$I_{VV} (\psi = \pi/2)$	$\langle \beta_{ZZZ}^2 \rangle$	$\langle \gamma_{ZZZZ}^2 \rangle$
$I_{HV} (\psi = 0)$	$\langle \beta_{ZXX}^2 \rangle$	$\langle \gamma_{ZXXX}^2 \rangle$

For a non-polarized incident signal,⁴

$$\beta_{SHS} = \sqrt{\langle \beta_{ZZZ}^2 \rangle + \langle \beta_{ZXX}^2 \rangle}$$

$$DR_{SHS} = \frac{\langle \beta_{ZZZ}^2 \rangle}{\langle \beta_{ZXX}^2 \rangle}$$

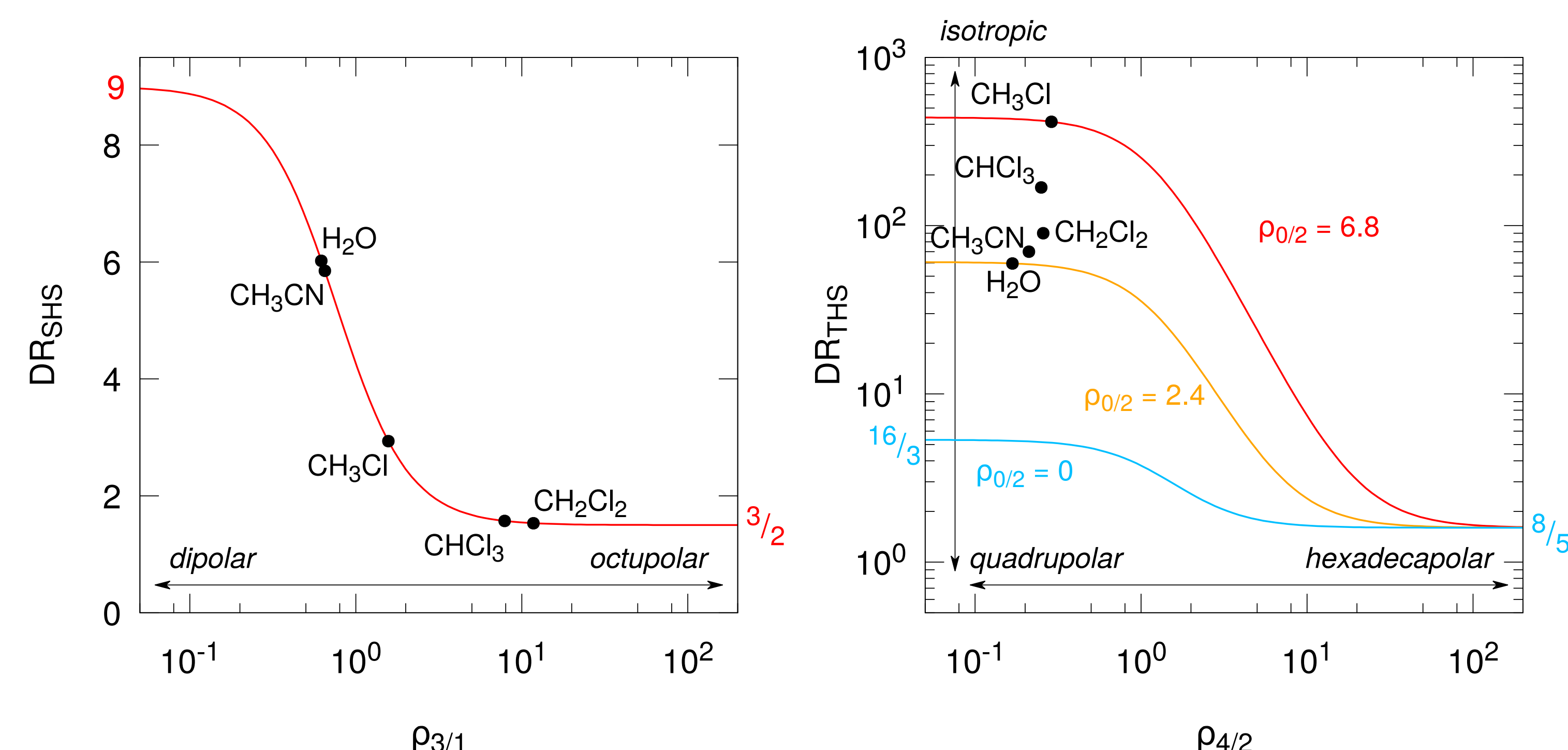
$$\gamma_{THS} = \sqrt{\langle \gamma_{ZZZZ}^2 \rangle + \langle \gamma_{ZXXX}^2 \rangle}$$

$$DR_{THS} = \frac{\langle \gamma_{ZZZZ}^2 \rangle}{\langle \gamma_{ZXXX}^2 \rangle}$$

β and γ tensors can also be decomposed into irreducible spherical components.⁵ Assuming Kleinman conditions, the β tensor is decomposed into dipolar ($J = 1$) and octupolar ($J = 3$) components and the γ tensor is decomposed into isotropic ($J = 0$), quadrupolar ($J = 2$) and hexadecapolar ($J = 4$) components. Assuming $\rho_{3/1} = |\beta_{J=3}|/|\beta_{J=1}|$, $\rho_{0/2} = |\gamma_{J=0}|/|\gamma_{J=2}|$ and $\rho_{4/2} = |\gamma_{J=4}|/|\gamma_{J=2}|$,

$$DR_{SHS} = \frac{18 \rho_{3/1}^2 + 63}{12 \rho_{3/1}^2 + 7}$$

$$DR_{THS} = \frac{32 \rho_{4/2}^2 + 252 \rho_{0/2}^2 + 144}{20 \rho_{4/2}^2 + 27}$$



	CCl ₄	CH ₂ Cl ₂	CHCl ₃	CH ₃ Cl	CH ₃ CN	H ₂ O
β_{SHS}	15.63	13.41	16.32	12.32	16.74	9.87
DR _{SHS}	1.50	1.53	1.57	2.94	5.87	6.01
$\rho_{3/1}$	$\sim \infty$	11.75	7.88	1.57	0.65	0.62
γ_{THS}	12719	8474	10993	5065	4037	1801
DR _{THS}	5744	90	169	414	70	60
$\rho_{0/2}$	$\sim \infty$	3.089	4.280	6.823	2.677	2.437
$\rho_{4/2}$	$\sim \infty$	0.257	0.250	0.288	0.211	0.168

These analyses are confirmed for dynamic quantities (about 30 and 10 % of increase at 1064 nm for β_{SHS} and γ_{THS} , respectively, and the DR are mostly unaffected).

- Comparison with dynamic γ_{THS} calculations (at 1300 nm) and experimental liquid phase results : CH₃CN (Experimental/gas phase calculated ratio of 1.49), CH₂Cl₂ (1.11), CHCl₃ (0.97) and CCl₄ (1.02). The experimental increase of γ_{THS} with the number of chlorine is reproduced by the calculation. This also suggests that the solvation effect are smaller for γ_{THS} than for β_{SHS} .

Outlook

Impact of solvation, Kleinman conditions (on the tensor decomposition), and amplitude of the vibrational contributions still need to be investigated.

Acknowledgements

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